

# PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 22.07.1999 (72)Inventor : ANDO KOJI

## (54) PURIFICATION OF COPPER SULFATE

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain high-purity copper sulfate with nickel content being a specific level or lower by such a practice that an aqueous solution of crude copper sulfate containing nickel as an impurity is heated to a specified temperature or higher, and copper sulfate separated and sedimented is then collected and subsequently dissolved in water again, and the resultant aqueous solution is concentrated to effect recrystallization of the objective copper sulfate.

**SOLUTION:** This high-purity copper sulfate is obtained by the following procedure: an aqueous solution of nickel-contg. copper sulfate is heated to 80° C, and copper sulfate separated and sedimented is then collected and subsequently dissolved in water again, and the resultant aqueous solution is concentrated to effect recrystallization, thus obtaining the objective copper sulfate 0.001 wt.% in nickel content; for example, the procedure is as follows: pure water is added to 1.3 kg of copper sulfate to prepare a 2L aqueous solution, which is heated under vigorous agitation; after complete dissolution of the copper sulfate, the aqueous solution is kept at 85° C for 4 h, thereby concentrated to 0.8 L, the resultant yellow-green precipitate is filtered and separated; the precipitate is then dissolved in water again and subsequently recrystallized, thus affording the objective high-purity copper sulfate 0.0004 wt.% in nickel content in a single step concentration; wherein the pH of the aqueous copper sulfate solution prior to heating is pref. 1.7-4.5 and the upper limit of heating temperature is the boiling point 100-110° C at the atmospheric pressure.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention is a refining method of the copper sulfate which removes nickel from copper sulfate containing nickel efficiently, and obtains high grade copper sulfate.

#### [0002]

[Description of the Prior Art] In copper electrorefining, usually it increases rather than the copper quantity in which the direction of the copper eluted from an anode carries out electrocrystallization with a cathode about 1%, and it is necessary to remove the copper accumulated in the electrolysis solution. Although there is also the method of removing as a removing method of such surplus copper by electrolytic winning which uses an insoluble anode, there are demerits, like the quality of the electrolytic copper which electric power cost requires about 10 times compared with the usual electrolysis, and also is obtained is inferior.

[0003] An electrolysis solution is condensed and cooled and other removing methods also include the method of separating the copper sulfate which deposits by supersaturation as a crystal of five monohydrates. In this case, the copper sulfate obtained has a use which can count also upon sale, such as using it for agriculture as the liquid component and the object for sterilization of plating liquid, and can be called advantageous removing method as a removing method of surplus copper.

[0004] However, when selling a copper sulfate crystal to outside companies, the impurity contained poses a problem. Most impurities have adhered to the crystal of copper sulfate, and by carrying out pH adjustment in the stage before concentration, or washing the surface with pure water etc. after a crystal, it can remove easily and does not become a problem. However, since it is an impurity in which it conflicts in an impurity and reason nickel is most kept at arm's length to plating of an electronic industry material, in order to use it for these uses, it is necessary to lose nickel dignity even to

about 1/100 grace as compared with about 0.001 or less % of the weight and usual copper sulfate, for example. However, the effective method was not able to say the method of decreasing the amount of nickel with concentration and a crystal, since the action of nickel is almost the same as that of copper and the amount of [ which carries out an eutectoid to copper in addition to adhesion in a crystal surface ] nickel is also large.

[0005]Therefore, conventionally, in order to obtain high grade copper sulfate with little nickel, it was required for there to be much further 2 to 3 times or more, and to repeat the process of concentration and a crystal from usual copper sulfate, and it was remarkably disadvantageous in respect of the manufacturing cost, the capacity utilization rate, the man day, the product yield, etc.

[0006]

[Problem(s) to be Solved by the Invention]This invention removes economically adhesion thru/or the nickel which carried out the eutectoid to copper sulfate as mentioned above, and the copper sulfate which obtains copper sulfate of a high grade makes refining method offer.

[0007]

[Means for Solving the Problem]In order to solve the above-mentioned technical problem, in this invention, copper sulfate which contains nickel as an impurity is dissolved as solution, A nickel content used a refining method of copper sulfate which is 0.001 or less % of the weight by collecting copper sulfate which carries out separation sedimentation, when said solution is heated at not less than 80 \*\*, and making said copper sulfate make remelt and condense and recrystallize further. In this method, the amount of [ under atmospheric pressure ] boiling point becomes a maximum substantially [ as for the pH of a copper sulfate aqueous solution before heating, it is preferred that it is / or more 1.7 / 4.5 or less, and / cooking temperature ].

[0008]

[Embodiment of the Invention]In order to remove conventionally the nickel contained as an impurity in copper sulfate, the effective method was found only by repeating remelting as mentioned above, but it had become a neck in the production process.

[0009]On the other hand, this invention persons found out that precipitate arose by [ in which air bubbles generate the solution of copper sulfate from liquid under atmospheric pressure ] continuing heating 80 \*\* at a not less than 85 \*\* elevated temperature preferably. The maximum of cooking temperature is the boiling point under atmospheric pressure, and is about 100-110 \*\* substantially. A solution condenses this precipitate, it is considered to be a thing with heterogeneous copper sulfate which becomes supersaturation and deposits, after said precipitate deposits, heating is stopped, and even if it cools to a room temperature, the crystal of copper sulfate by supersaturation is not produced.

[0010]When said precipitate was analyzed, distributing about 1% of the solutions before nickel heating also found out. That is, high grade copper sulfate with little nickel can be obtained by collecting these precipitate, dissolving again and depositing the crystal of copper sulfate, without needing a reagent special in addition to heating etc.

[0011]if it will not generate whether this crystal is remelted if the pH of the copper sulfate solution before heating becomes lower in general than 1.7, and pH exceeds 4.5 in general, copper will precipitate as copper hydroxide, and precipitate of nickel hydroxide will also be generated, and the refining effects will be lost -- the thing header was carried out.

[0012]If it adjusts so that sulfuric acid etc. may be \*\*\*\*(ed) and it may become lower than 1.7 about pH even if precipitate generates, precipitate will remelt. Therefore, the pH of the solution before heating is preferred when or more 1.7 the thing to do to 4.5 or less carries out this invention.

[0013]

[Example](EXAMPLE) Pure water was added to 1.3 kg of copper sulfate crystals, and the bottom carried out thing preparation and it was made 2 l. with the solution A. pH of A was 2.0. It heated strong-stirring so that air may involve in A, after the dissolution was thoroughly maintained at not less than 85 \*\* for 1 hour, and liquid was evaporated to 1.9 l. Even if it cooled as it is by the concentration at this time, although not supersaturation but the crystal should not deposit, in order that the yellow-green precipitate B might generate a solubility top, it filtered this, and separated and analyzed it.

[0014]It condensed to 0.8 l. over 3 hours after that. Heating was stopped stirring after concentration and it cooled to ordinary temperature over 2 hours. After-cooling solid-liquid was separated, the after-cooling concentrate was set to C, Cu and nickel were analyzed, and the Cu/nickel ratio was calculated.

[0015]As shown in Table 1, nickel was hardly contained in the precipitate B which heated A and deposited, but high grade copper sulfate (copper sulfate D) with very as little nickel as [ 0.0004 % of the weight ] was obtained by the copper sulfate which made this precipitate remelt and recrystallize, i.e., a real target, by one step of concentration.

[0016]Although the pH of the solution was changed and the equivalent examination was done further, It turned out that it does not generate whether pH at the time of the dissolution remelts this crystal or less by 1.7 in general, and copper precipitates as copper hydroxide, and pH also generates precipitate of nickel hydroxide or more by 4.5 in general, and the refining effects are lost. When it adjusted so that sulfuric acid etc. might be \*\*\*\*(ed) and it might become 1.7 or less about pH even if precipitate generated, it also checked collectively that precipitate remelted.

(Comparative example) What added pure water to 1.3 kg of copper sulfate crystals like the example, and was 2 l. was prepared, and it was considered as the solution A of H2.0. It stirred slowly, covering a container in a comparative example, so that the

solution A may not consider contamination of air as evaporation, and dissolved thoroughly at about 70 \*\*. No precipitate was generated at this time. It condensed to 0.8 l. over 3 hours after that. Heating was stopped stirring after concentration and it cooled to ordinary temperature over 2 hours. After-cooling solid-liquid was separated, Cu and nickel were analyzed, respectively, and the Cu/nickel ratio was calculated. The precipitating copper sulfate crystal was set to E, and the concentrate was set to F. [0017]the copper sulfate crystal E -- again - the recrystallization copper sulfate G obtained by condensing was analyzed and compared. Furthermore this recrystallization copper sulfate was recrystallized further, and the third-time crystal copper sulfate H was obtained.

[0018]

(表1)

	单位	Cu	Ni	Cu/Ni
水溶液A	g/l	163	0.256	640
(実施例)				
生成沈殿B	wt%	52.4	0.0014	37430
濃縮後液C	g/l	21.9	0.18	120
再結晶硫酸銅D	wt%	25.5	0.0004	63750
(比較例)				
硫酸銅結晶E	wt%	25.5	0.04	640
濃縮液F	g/l	41.4	0.032	1290
再結晶硫酸銅G	wt%	25.5	0.004	6380
再々結晶硫酸銅H	wt%	25.5	0.0004	63750

As shown in Table 1, nickel is hardly contained in the precipitate B which deposited by A, but making this precipitate remelt and recrystallize, i.e., high grade copper sulfate with very as little nickel as [ 0.0004% ] is substantially obtained by one step of concentration, understands. On the other hand, by the conventional method, three concentration and recrystallization were required to acquire the same nickel grace.

[0019]Although it made to obtain a high grade copper sulfate crystal with few nickel contents into the key objective in this invention, as shown in Table 1, it is effective in the copper sulfate solution which nickel condensed after the crystal deposit being obtained.

[0020]

[Effect of the Invention]The copper sulfate crystal of a high grade with little nickel comes to be economically obtained by this invention.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1]A refining method of copper sulfate collecting copper sulfate which heats in the atmosphere a copper sulfate aqueous solution which dissolved said copper sulfate at not less than 80 \*\*, and carries out separation sedimentation in a refining method of copper sulfate containing nickel, and making said copper sulfate remelt and recrystallize.

[Claim 2]A refining method of the copper sulfate according to claim 1, wherein nickel grace in refined copper sulfate is 0.001 or less % of the weight.

[Claim 3]A refining method of the copper sulfate according to claim 1 or 2, wherein the pH of a copper sulfate aqueous solution before heating is 1.7 or more and 4.5 or less.

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(54)【発明の名称】 硫酸銅の精製方法

(57)【要約】

【課題】 Niを含む硫酸銅の精製において、Ni分の少ない硫酸銅を経済的に精製する方法を提供する。

【解決手段】 ニッケルを含む硫酸銅を水溶液とし、これを80°C以上に加熱し、このとき分離沈降してくる硫酸銅結晶を回収し、濃縮再結晶させることによって、ニッケルの含有量の少ない硫酸銅が得られる。

## 【特許請求の範囲】

【請求項1】ニッケルを含む硫酸銅の精製方法において、前記硫酸銅を溶解した硫酸銅水溶液を大気中で80°C以上に加熱して分離沈降してくる硫酸銅を回収し、前記硫酸銅を再溶解し再結晶させることを特徴とする硫酸銅の精製方法。

【請求項2】精製された硫酸銅中のニッケル品位が0.001重量%以下であることを特徴とする請求項1記載の硫酸銅の精製方法。

【請求項3】加熱前の硫酸銅水溶液のpHが1.7以上、4.5以下であることを特徴とする請求項1または2に記載の硫酸銅の精製方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、ニッケルを含む硫酸銅から効率的にニッケルを除去し、高純度な硫酸銅を得る硫酸銅の精製方法である。

## 【0002】

【従来の技術】銅の電解精製に於いては、アノードから溶出する銅の方がカソードで電析する銅量よりも1%程度多くなるのが普通であり、電解液に蓄積した銅を除去することが必要となる。このような余剰銅の除去方法としては、不溶性のアノードを使用した電解採取により除去する方法もあるが、電力コストが通常の電解に比べて10倍程度も要する上に、得られる電気銅の品質が劣るなどの短所がある。

【0003】また、その他の除去方法として、電解液を濃縮・冷却し、過飽和によって析出する硫酸銅を5水塩の結晶として分離する方法もある。この場合得られる硫酸銅は、めっき液の液成分や殺菌用として農業用に使用するなど販売も見込める用途があり、余剰銅の除去方法としては、有利な除去方法といえる。

【0004】しかし、硫酸銅結晶を外販する場合、含まれる不純物が問題となる。大部分の不純物は硫酸銅の結晶に付着しているものであり、濃縮前の段階でpH調整したり結晶後に表面を純水等で洗浄することにより容易に除去でき、問題とはならない。しかし、不純物のなかでもとりわけニッケルは電子材料のめっきに対してもっとも敏感される不純物であるため、これらの用途に使用するには、例えば、Ni品位を0.001重量%以下程度と通常の硫酸銅に比較して100分の1程度の品位にまで下げる必要となる。しかしながら、Niは、その挙動が銅とほぼ同じであり、結晶表面への付着以外に銅と共析するニッケル分も多いことから濃縮・結晶によって、Ni量を減少させる方法は、効果的な方法とはいえない。

【0005】よって、従来はニッケルの少ない高純度な硫酸銅を得るためには、濃縮・結晶の工程を通常の硫酸銅よりもさらに2~3回以上多く繰り返すことが必要であり、製造コスト・設備稼働率・工数・製品収率等の点

で著しく不利であった。

## 【0006】

【発明が解決しようとする課題】本発明は上記のように硫酸銅に付着ないし共析したニッケルを経済的に除去し、高純度の硫酸銅を得る硫酸銅の精製方法提供するものである。

## 【0007】

【課題を解決するための手段】上記の課題を解決するために、本発明では、ニッケルを不純物として含む硫酸銅を水溶液として溶解させ、前記水溶液を80°C以上に加熱したときに分離沈降してくる硫酸銅を回収し、さらに前記硫酸銅を再溶解させ、濃縮、再結晶させることにより、ニッケル含有量が0.001重量%以下である硫酸銅の精製方法を用いた。また、この方法において、加熱前の硫酸銅水溶液のpHは、1.7以上4.5以下であることが好ましく、加熱温度は、実質的に大気圧下での沸点相当が上限となる。

## 【0008】

【発明の実施の形態】従来、硫酸銅中に不純物として含まれるニッケルを除去するためには、前述のように再溶解を繰り返すことしか有効な方法が見当たらず、生産工程でのネックになっていた。

【0009】これに対して、本発明者らは、硫酸銅の溶液を大気圧下で液から気泡が発生する80°C、好ましくは85°C以上の高温で加熱し続けることにより、沈殿が生じることを見出した。なお、加熱温度の上限は、大気圧下での沸点であり、実質的に100~110°C程度である。この沈殿は、溶液が濃縮して過飽和になって析出する硫酸銅とは異質の物と考えられ、前記沈殿が析出した後に加熱を止め、室温まで冷却しても過飽和による硫酸銅の結晶は生じない。

【0010】さらに、前記沈殿を分析してみると、ニッケルが加熱前の溶液の1%ほどしか分配しないことも見出した。すなわち、この沈殿を回収し再度溶解して硫酸銅の結晶を析出させることにより、加熱以外に特別な試薬等も必要とせずに、ニッケルの少ない高純度な硫酸銅を得ることができる。

【0011】また、加熱前の硫酸銅溶液のpHが、おおむね1.7より低くなると、この結晶は再溶解するのか生成せず、またpHがおおむね4.5を超えると、銅が水酸化銅として沈殿すると共に水酸化ニッケルの沈殿も生成し、精製効果がなくなること見出した。

【0012】また、沈殿が生成しても硫酸等を補加してpHを1.7より低くなるように調整すると沈殿が再溶解する。よって、加熱前の水溶液のpHは、1.7以上4.5以下とすることが本発明を実施する上で好ましい。

## 【0013】

【実施例】(実施例)硫酸銅結晶1.3kgに純水を50加え2リットルにしたもの用意し、水溶液Aとした。Aのp

Hは、2.0であった。Aをエアーが巻き込むように強攪拌しながら加熱し、完全に溶解後も85°C以上に1時間維持し、液を1.9リットルまで蒸発させた。なお、この時の濃度ではそのまま冷却しても溶解度上は過飽和でなく結晶は析出しないはずであるが、黄緑色の沈殿Bが生成するためこれを濃縮して分離し分析した。

【0014】その後3時間をかけて、0.8リットルまで濃縮した。濃縮後攪拌しながら加熱を止め、2時間かけて常温まで冷却した。冷却後固液を分離し、冷却後濃縮液をCとして、CuとNiを分析し、Cu/Ni比を求めた。

【0015】表1に示すように、Aを加熱して析出した沈殿Bには殆どニッケルが含まれておらず、この沈殿を再溶解して再結晶させた硫酸銅、すなわち実質的に1段の濃縮でNiが0.0004重量%と極めて少ない高純度な硫酸銅（硫酸銅D）が得られた。

【0016】なお、同等の試験を溶解液のpHを変化させてさらに行つたが、溶解時のpHがおおむね1.7以下ではこの結晶は再溶解するのか生成せず、またpHがおおむね4.5以上では、銅が水酸化銅として沈殿すると共に水酸化ニッケルの沈殿も生成し、精製効果がなくなることがわかった。また、沈殿が生成しても硫酸等を補加してpHを1.7以下になるように調整すると沈殿が再溶解することも併せて確認した。

（比較例）実施例と同様に硫酸銅結晶1.3kgに純水を加え2リットルにしたもの用意しH2.0の水溶液Aとした。比較例において水溶液Aは、蒸発とエアーの巻き込みをしないように容器に蓋をしたままゆっくりと攪拌し、70°C程度で完全に溶解した。このとき、沈殿等は何も生成しなかった。その後3時間をかけて0.8リットルまで濃縮した。濃縮後攪拌しながら加熱を止め、2時間かけて常温まで冷却した。冷却後固液を分離し、それぞれCuとNiを分析し、Cu/Ni比を求めた。沈

殿した硫酸銅結晶をE、濃縮液をFとした。

【0017】また、硫酸銅結晶Eを再度・濃縮し、得られた再結晶硫酸銅Gを分析して比較した。さらにこの再結晶硫酸銅をさらに再結晶して再々結晶硫酸銅Hを得た。

【0018】

（表1）

	単位	Cu	Ni	Cu/Ni
水溶液A	g/l	163	0.256	640
（実施例）				
生成沈殿B	wt%	52.4	0.0014	37430
濃縮後液C	g/l	21.9	0.18	120
再結晶硫酸銅D	wt%	25.5	0.0004	63750
（比較例）				
硫酸銅結晶E	wt%	25.5	0.04	640
濃縮液F	g/l	41.4	0.032	1290
再結晶硫酸銅G	wt%	25.5	0.004	6380
再々結晶硫酸銅H	wt%	25.5	0.0004	63750

表1に示すようにAで析出した沈殿Bには殆どニッケルが含まれておらず、この沈殿を再溶解し再結晶させると、すなわち実質的に1段の濃縮でNiが0.0004%と極めて少ない高純度な硫酸銅が得られることがわかる。これに対して従来の方法では同じNi品位を得るのに3回の濃縮・再結晶が必要であった。

【0019】なお、本発明では、ニッケル含有量の少ない高純度硫酸銅結晶を得ることを主目的としたが、表1に示すように、結晶析出後にニッケルの濃縮した硫酸銅溶液が得られる効果もある。

【0020】

【発明の効果】本発明によりニッケルの少ない高純度の硫酸銅結晶が経済的に得られるようになる。